

The present invention relates to the field of generators of hydrogen, a gas widely used as fuel or reducing agent in numerous devices or industrial processes.

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A more specific subject-matter of the invention is novel solid compositions which can decompose with the generation of hydrogen according to a self-sustaining combustion reaction, and the use of these compositions for supplying hydrogen to proton exchange membrane fuel cells.

Numerous solid compositions which generate hydrogen by combustion are known, in particular for producing hydrogen intended to act as fuel in chemical lasers.

Patent US 3 948 699 discloses solid compositions which generate hydrogen by combustion composed of a mixture of alkali metal borohydride, for example sodium borohydride NaBH_4 , with a metal oxide, for example iron oxide Fe_2O_3 .

However, the yields by mass of hydrogen produced are low, less than 5%, expressed by weight of hydrogen obtained with respect to the total weight of the composition.

Patent US 4 064 225 discloses other solid compositions which generate hydrogen by combustion composed of a mixture of alkali metal borohydride, for example sodium borohydride, with ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ or ammonium dichromate $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

The yields by mass are slightly higher, of the order of 6%.

Such hydrogen yields, less than or in the vicinity of 5%, prove in practice to be inadequate, in particular when miniaturization of systems is desired, for example

when it is desired to replace the batteries of portable electronic systems, such as telephones and computers, with miniature hydrogen fuel cells.

5 Patent US 4 673 528 discloses a solid hydrogen-generating composition which can be in the form of pellets which can be used as fuels in chemical lasers. The hydrogen-generating compositions disclosed in this
10 patent are thermally stable and comprise, as percentage by mass, between 5 and 15% of an oxidizing agent chosen from lithium nitrate LiNO_3 and potassium nitrate KNO_3 , from 80 to 90% of magnesium borohydride diammoniate $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ and optionally from 2 to 15% of a binder, such as polytetrafluoroethylene. The hydrogen yields
15 obtained with this type of composition can reach 12.5%.

A person skilled in the art who wishes to replace the batteries of portable electronic systems, such as telephones and computers, with miniature hydrogen fuel
20 cells is continually preoccupied with trying to find novel solid compositions which generate hydrogen by combustion which are completely stable and which provide better yields by mass of hydrogen.

25 The present invention provides a solution to this problem.

A more specific subject-matter of the invention is novel solid compositions which can decompose with the
30 generation of hydrogen according to a self-sustaining combustion reaction after initiation of this reaction by an appropriate heat source, the said composition comprising an alkali metal borohydride or alkaline earth metal borohydride and, as oxidizing salt,
35 strontium nitrate $\text{Sr}(\text{NO}_3)_2$.

It has been found, unexpectedly, that such compositions make it possible to provide a yield by mass of hydrogen which can reach 12% depending on the nature and the

relative proportions of the constituents, which constitutes a particularly advantageous technical and economic advance for the abovementioned reasons.

- 5 According to a preferred alternative form, the compositions according to the invention are devoid of organic matter, that is to say that they are composed solely of inorganic compounds.
- 10 In a particularly preferred way, they are composed essentially of an alkali metal borohydride or alkaline earth metal borohydride and of strontium nitrate $\text{Sr}(\text{NO}_3)_2$, that is to say that these constituents are the predominant ones by weight. It will be appreciated that
- 15 the sum of the contents by weight of alkali metal borohydride or alkaline earth metal borohydride and of strontium nitrate $\text{Sr}(\text{NO}_3)_2$ is greater than or equal to 75%, better still greater than or equal to 90% and even greater than or equal to 95%, with respect to the total
- 20 weight of the composition.

Compositions composed solely of alkali metal borohydride or alkaline earth metal borohydride and of strontium nitrate $\text{Sr}(\text{NO}_3)_2$, that is to say for which the

25 sum of the contents by weight of the two constituents reaches 100%, are particularly preferred. The term "composed solely" should be understood as meaning that the compositions can nevertheless include the impurities present in the crude or purified alkali

30 metal borohydride or alkaline earth metal borohydride and in the crude or purified $\text{Sr}(\text{NO}_3)_2$ salt used, or alternatively additives, such as stabilizers, whether these products are commercially available or are synthesized according to conventional methods.

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When the compositions are not composed solely of alkali metal borohydride or alkaline earth metal borohydride and of strontium nitrate $\text{Sr}(\text{NO}_3)_2$, they can, for example, also comprise other metal, alkali metal or

alkaline earth metal borohydrides and/or a metal hydride and/or other oxidizing inorganic salts, such as alkali metal nitrates, ammonium sulphate, ammonium dichromate and iron oxides.

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According to another preferred alternative form of the invention, the alkali metal borohydride is chosen from the group consisting of lithium borohydride, sodium borohydride and their mixtures.

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According to another preferred alternative form of the invention, the alkaline earth metal borohydride used can be magnesium borohydride $Mg(BH_4)_2$, which has available a high level of hydrogen.

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Generally and preferably, according to the invention, the ratio of content by weight of alkali metal borohydride or alkaline earth metal borohydride to content by weight of strontium nitrate is between 1 and 10, better still between 2 and 10 and preferably between 4 and 10.

One aim of the invention is to obtain hydrogen-generating compositions having a good yield by mass of hydrogen per gram of solid composition and which are combusted at a temperature which is sufficiently high for the reaction to be self sustaining and to prevent the solid composition from being extinguished and thus from being entirely consumed. The relative proportions by weight between the oxidizing agent and the reducing agent should be established so as to achieve this aim.

According to another preferred alternative form, the solid compositions according to the invention are provided in the form of a compact material having a specific form, for example and preferably in the form of pellets or grains. The grains can have any shape, preferably spherical, ovoid or cylindrical.

The pellets can also have any thickness and any peripheral geometry, for example circular, elliptical, square or rectangular.

- 5 The thickness of the pellets may not be constant.

The solid compositions according to the invention can be obtained by analogy with the described methods used to produce the abovementioned solid compositions of the
10 state of the art, for example by simple mixing of the constituents, milling and then mechanical homogenization. It is also possible to mill the constituents before the mixing or alternatively to use constituents already in pulverulent form.

15 The compositions can also be obtained by granulation.

When, preferably, it is desired to obtain a solid composition which is provided in the form of a compact material, the granular or pulverulent homogeneous
20 mixture of the various constituents can, for example, be agglomerated by compacting in a pressing container having the shape and the dimensions which are desired for the compact material.

25 It is also possible to obtain a compact material by dissolving and/or suspending the constituents in a liquid medium. After homogenizing and placing in a mould with the appropriate dimensions desired for the
30 compact material, the liquid is removed, for example by evaporation, which makes it possible to obtain a compact material.

Another subject-matter of the present invention is a
35 process for the generation of hydrogen by self-sustaining combustion of a solid composition comprising an alkali metal borohydride or alkaline earth metal borohydride and, as oxidizing salt, strontium nitrate $\text{Sr}(\text{NO}_3)_2$.

According to this process, a pulverulent or granular homogeneous solid composition comprising an alkali metal borohydride or alkaline earth metal borohydride and strontium nitrate $\text{Sr}(\text{NO}_3)_2$ is first of all prepared.

This composition is subsequently agglomerated using appropriate means, for example those mentioned above, so as to form a compact material, and then the compact material is placed in a combustion chamber which is purged under an inert gas or placed under vacuum.

When the dead volume (the volume remaining in the chamber after the compact material has been placed therein) is low, such a purge may in practice be unnecessary.

The combustion of the compact material is then initiated using an appropriate heat source, which brings about the self-sustaining combustion of the material with generation of hydrogen up to the end of the combustion.

The appropriate heat sources which make possible the initiation of the combustion by the "Joule" effect are well known to a person skilled in the art, in particular electrical initiators. The use of a nickel-chromium ignition filament placed in contact or coated with the composition to be initiated, on which a sufficient voltage and a sufficient current intensity (and therefore a sufficient power) are imposed, is entirely suitable. It is possible, for example, for a given voltage, to increase the intensity of the current until the combustion is initiated.

In some cases, to promote the ignition, a conventional relay-ignition powder well known to a person skilled in the art can be positioned between the filament and the compact material. In this case, use will preferably be

made of a relay-ignition powder of the same nature as the compact material according to the invention, that is to say having the same constituents but with a markedly lower ratio of content by weight of alkali metal borohydride or alkaline earth metal borohydride to content by weight of strontium nitrate $\text{Sr}(\text{NO}_3)_2$, for example between 0.1 and 1.

Another subject-matter of the present invention is a pyrotechnic hydrogen generator, intended to supply hydrogen to a proton exchange membrane fuel cell, comprising an abovementioned solid composition according to the invention.

Fuel cells operating with hydrogen, also known as proton exchange membrane fuel cells, are well known to a person skilled in the art.

Such a fuel cell is composed essentially of 2 parts:

- the core of the fuel cell, composed of one or more electrochemical cells mounted in series, which produces the electrical energy;
- the fuel, namely hydrogen, reservoir.

Attached to these two main parts are auxiliary systems relating in particular to supplying hydrogen to the core of the fuel cell, to discharging the water produced or to cooling.

An electrochemical cell of the core of the fuel cell is represented diagrammatically in Figure 1.

It is observed, in this Figure 1, that an electrochemical cell 1 of the core of the fuel cell supplies electrical energy from two electrochemical reactions carried out on two electrodes 2 and 3 generally composed of carbon and separated by a proton exchange membrane 4 acting as electrolyte and generally composed of fluoropolymers impregnated with water. Hydrogen H_2

is oxidized on the anode 2 in the presence of a generally platinum-based catalyst, the hydrogen being separated into protons H^+ and electrons e^- . The stream of protons H^+ passes through the membrane 4, while the
5 electrons e^- , which are not able to pass through the membrane 4, are captured by a current collector 5 connected to an external electrical circuit 6 to rejoin the cathode 3. On the other side of the membrane 4, at the cathode 3, the protons H^+ and the electrons e^-
10 recombine with oxygen O_2 , generally originating from the surrounding air, to produce water H_2O .

The pyrotechnic hydrogen generators according to the invention are essentially composed of one or more
15 chambers in which a solid composition according to the invention, separate means for initiating the combustion of the composition in each of the chambers, means for actuating this initiation and means for transferring the hydrogen released in the chambers to the anode of a
20 cell of the core of the fuel cell are placed.

Preferably, the overall amount of hydrogen capable of being supplied by the generator is released discontinuously by a separate initiation of the solid
25 compositions present in the various chambers. The mass of solid composition in each chamber can be identical or different from one chamber to another. The last alternative form makes possible release of hydrogen in an amount suited to a specific need.

30 The various chambers can emerge in a chamber for the expansion of the hydrogen released, this chamber being connected to the anode compartment of a cell or having one of its walls at least partially formed by the
35 anode.

Another subject-matter of the present invention is a proton exchange membrane fuel cell using hydrogen as fuel, comprising at least one electrochemical cell and

one abovementioned pyrotechnic hydrogen generator according to the invention connected to the anode compartment of the cell.

- 5 The following nonlimiting examples illustrate the invention and the advantages which it provides.

Example 1 Solid composition composed of a mixture of NaBH_4 and of $\text{Sr}(\text{NO}_3)_2$ in the relative proportions by weight 60/40 respectively

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A mixture of 90 g of NaBH_4 and 60 g of $\text{Sr}(\text{NO}_3)_2$ is milled and then homogenized.

- 15 A fraction of the pulverulent and homogeneous mixture thus obtained is subsequently introduced into and then compacted in the compression die of a pelletizer having the desired pellet geometry, under a pressure of 10^7 Pa (100 bar).

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The circular pellet thus obtained, with a diameter of 5 mm and a mass of 80 mg, is subsequently introduced into a combustion chamber with a volume of 10 cm^3 and equipped with a pressure gauge, a temperature probe and

25 a conventional ignition device comprising a nickel (80 weight%)-chromium (20 weight%) filament. The pellet is brought into contact with the filament and then the chamber is purged with an inert gas (nitrogen) under an absolute pressure of 10^5 Pa (1 bar).

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The filament is subsequently heated by the Joule effect until initiation of the combustion.

- Once initiated, the combustion of the composition is
- 35 self-sustaining and lasts approximately 3 s.

The combustion temperature, measured experimentally from the maximum pressure, varies between 480 and 600°K approximately following the firings.

On completion of the combustion, the chamber is allowed to cool to ambient temperature and then the pressure in the chamber is recorded.

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The measured increase in pressure and the analysis of the gases present after combustion by chromatography coupled to a mass spectrometer makes it possible to calculate a yield by mass of hydrogen of 5.32 to 5.88%,
10 expressed as grams of hydrogen released per gram of solid composition.

DTA analyses were carried out on this composition formed of 60/40 sodium borohydride NaBH_4 and $\text{Sr}(\text{NO}_3)_2$ to
15 determine whether it was stable.

DTA (Differential Thermal Analysis) is a calorimetric measurement test. It consists in heating the composition from 15 to 200°C , the temperature being
20 increased by 8°C per minute. During this rise in temperature, this test consists in plotting the temperatures of the endothermic or exothermic peaks and in measuring the energy released or absorbed. If no
25 energy is released or absorbed, this means that the composition is stable and thus that the constituents of the composition analysed are entirely compatible.

The tests carried out on the composition of Example 1, 60/40 $\text{NaBH}_4/\text{Sr}(\text{NO}_3)_2$, show that this composition is
30 stable. This is because, during the DTA test, no energy was released or absorbed during the rise in temperature.

Examples 2 to 8 are carried out in exactly the same
35 way, only the relative proportions by weight between the two constituents being modified.

For each of Examples 1 to 7, the results obtained experimentally, on the one hand, and the results

obtained by calculations, on the other hand, are shown in Table 1 below. Two or three tests were carried out for each of the examples but only the mean result appears. For some of the examples, no experiment has yet been carried out and therefore only the results obtained theoretically appear.

	$\text{NaBH}_4/\text{Sr}(\text{NO}_3)_2$ ratio by mass	Theoretical yield of hydrogen (%)	Experimental yield of hydrogen (%)
Example 1	65/35	6.93	4.55
Example 2	60/40	6.39	5.90
Example 3	55/45	5.86	5.75
Example 4	50/50	5.33	-
Example 5	40/60	4.2	-
Example 6	30/70	3.0	-
Example 7	20/80	0.47	-

Table 1

- 10 The theoretical yield of hydrogen decreases, of course, when the proportion of hydrogen-carrying reducing agent decreases. However, the measured yield only corresponds to the theoretical yield for sufficiently high values of combustion temperatures.

Examples 8 to 14 Solid compositions composed of a mixture of LiBH_4 and $\text{Sr}(\text{NO}_3)_2$ in different relative proportions by weight.

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In this example, sodium borohydride NaBH_4 is replaced by lithium borohydride LiBH_4 . The preparation is carried out in exactly the same way as in Example 1 described above, that is to say with the production of
10 a pellet with the same mass. As in Examples 1 to 7 above, the relative proportions by weight between the two constituents are varied.

The theoretical results calculated for the various
15 compositions are displayed in Table 2 below:

	$\text{LiBH}_4/\text{Sr}(\text{NO}_3)_2$ ratio by mass	Combustion temperature (°K)	Yield of hydrogen (%)
Example 8	70/30	265	11.20
Example 9	60/40	743	10.20
Example 10	50/50	1251	9.26
Example 11	40/60	1491	7.40
Example 12	30/70	1680	5.53
Example 13	20/80	2048	3.58
Example 14	10/90	2392	0.02

Table 2

The tests carried out on the composition of Example 9,
20 60/40 $\text{LiBH}_4/\text{Sr}(\text{NO}_3)_2$, show that this composition is not completely stable. This is because, during the DTA test, an energy absorption of 112 J/gram was observed

between 113 and 124°C.

Examples 15 to 22

5 In these examples, an alkali metal borohydride, such as NaBH₄ or LiBH₄, is no longer used but rather an alkaline earth metal borohydride, Mg(BH₄)₂, and strontium nitrate Sr(NO₃)₂ is still used as oxidizing agent. The preparation is carried out in the same way as in the preceding examples with different relative proportions by weight between the two constituents. The theoretical results obtained by calculations are displayed in Table 3 below.

	Mg(BH ₄) ₂ /Sr(NO ₃) ₂ ratio by mass	Combustion temperature (°K)	Yield of hydrogen (%)
Example 15	80/20	571	11.95
Example 16	70/30	1079	10.45
Example 17	60/40	1789	8.93
Example 18	50/50	1947	7.16
Example 19	40/60	2049	5.51
Example 20	30/70	2145	4.04
Example 21	20/80	2673	1.74
Example 22	10/90	2477	0.01

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Table 3

Measurements were carried out with a pellet having the two constituents with relative proportions by weight of the Mg(BH₄)₂ to the strontium nitrate Sr(NO₃)₂ of 70/30 respectively. A yield by mass of H₂, expressed as grams

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- 14 -

of hydrogen released per gram of solid composition, of 9.55% was obtained as results.